Discussion

The oil of the mamey seed is an important potential source of high quality vegetable oil for soaps and cosmetics as well as for other uses. At the present time, with the major part of the mamey crop being used as a fresh fruit for domestic consumption, it is impractical to collect the seed for oil production. While some unsuccessful attempts have been made to preserve the fruit, it is entirely possible that such a process will be developed, and in this event considerable quantities of otherwise useless waste product will be available for oil production from the seed. In addition, there is a substantial amount of wild mamey in various parts of Mexico that could be gathered for oil production from the seed. The tree is reputed to yield from 100 to 200 fruits per season. This yield, in view of the relatively high unit weight of the seed and its high oil content, makes the production of the oil from wild plants more feasible than from many other wild oil-bearing seeds, especially in those areas where the trees are not too widely scattered. Another possible source of the oil is from culls and overproduction in those areas now cultivating mamey for the fruit markets.

Summary

The physical and chemical characteristics of the oil of the fruit of the mamey [*Calocarpum mammosum* (*L.*) Pierre] have been reported.

The composition of the oil has been calculated.

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Modification of the Laboratory Centrifuge Method for the Determination of Refining Loss of Soybean Oil*

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COMMERCIAL refining of oils by the centrifugal method has given ample evidence of higher efficiencies and yields over the batch method. Difficulties encountered in the refining of certain extracted soybean oils by the Official A.O.C.S. cup method have stimulated considerable research and investigation on the development of a laboratory centrifugal method which would give results comparable to those obtained from commercial operations.

Most of the work has been done by the Refining Committee of the A.O.C.S. and through the efforts of this committee a number of centrifugal methods have been proposed and studied. The centrifugal method was an obvious choice because it permits compacting the soap stock, thus overcoming the effect of watery or sloppy foots, and results in efficient draining of the clear oil. The first proposal of a laboratory centrifugal method was that presented by the Swift and Company Research Laboratories (1). They reported the use of a centrifuge in refining tests as an aid in obtaining quicker and better separation of the foots. Refinings were made in accordance with the tentative cup method. A portion of the oil-foots mixture was then poured into a pear-shaped container and the container swirled in the centrifuge to settle and compact the foots. The clear oil was drained and weighed. The report of the Refining Committee 1941-1942 (2) covered a complete study of a modification of the suggested method. Much of this work was done by the Regional Soybean Laboratory which recommended the use of 30° Bé alkali in five times the theoretical amount necessary to neutralize the free fatty acid. The high Baume lye was considered necessary to avoid water in the oil to even a greater extent than when gravity settling was used. Refining was done in the bronze centrifugal trunion cups using the regular refining bath apparatus. Stirrer blades were cut to permit insertion into the cups and a wooden yoke fashioned to secure the cups in place. The oil was freed from the foots by centrifugation at 2,800 R.P.M. in an International Centrifuge size 1, Type SB.

This method was tested on six solvent extracted oils at the Regional Soybean Laboratory and two of these oils (No. 3 and No. 4) sent out as collaborative samples to six independent laboratories. Their results are tabulated in the committee's report. Conclusions drawn from the collaborative work are summarized as follows: "Inspection of the results reveals that neither of the samples tested caused the type of difficulty often encountered with the A.O.C.S. method with solvent extracted oils. For this reason they cannot be considered the most stringent test of the method as far as overcoming the difficulties of soft or sloppy foots. On sample No. 3 only three out of six laboratories checked well by the centrifugal method while all six agreed when the A.O.C.S. method was used. On sample No. 4 four out of six agreed well by the centrifuge method and with the A.O.C.S. method four out of six agreed well." Conclusions in the report were: "These results certainly do not constitute any overwhelming argument in favor of the centrifuge method. However, consideration should be given to the fact that the A.O.C.S. method is familiar and more standardized while the proposed method was being carried out for the first time with improvised equipment and unavoidable variations in cups and centrifuging."

The report of the Refining Committee (3) for 1942-1943 gives the results up to that date on work outlined at the previous meeting held April 24, 1940, at the Regional Soybean Products Laboratory. The report presents data on the refining of 12 oils by both the centrifugal and A.O.C.S. official methods. The statement is made that the centrifugal method has given firm foots for all oils and offers a sure

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means for evaluating an oil when the present official method fails. Data were also presented showing the effect of varying the amounts of alkali used in the refinings. Refining loss was found to increase with increase of alkali. Weaker alkalies gave lower refining losses than the equivalent amount of higher strength alkali.

In a later report (4) additional results were presented for the refining of four samples of clarified extracted, three extracted, eight expeller, and three hydraulic pressed soybean oils, by both the official method and centrifugal method. The committee was in agreement that: 1. The centrifuge method was quicker and always gave compact foots when recommended conditions were followed. 2. The centrifuge method losses were in general, similar to the lower losses obtained by the present official method. 3. The centrifuge method gives higher bleached colors with the 30°Bé alkali. Lower strength alkalies give bleached values similar to those obtained by the cup method. The attitude of the committee apparently changed during the following year as the report of the minutes of the October 5, 1943, meeting (5) contains the recommendation that "due to the difficulty encountered in obtaining equipment and to the disadvantages that showed up in the experimental work so far carried out, it was decided that the centrifugal method as presently constituted be dropped." Interest was expressed as to the possibility of getting a design for a centrifuge that would give laboratory results equivalent to those of the plant machines.

A subcommittee was appointed to contact a manufacturer in an effort to develop a satisfactorily designed centrifugal laboratory unit and an analytical procedure that would give reproducible results on all types of alkali refined oils. This subcommittee contacted the Sharples Corporation and later received a method and details of a centrifuge which had been built for special test work. Details of the design and method are given in the Report of the Refining Committee 1944-45 (6). The Sharples Centrifuge was said to permit greater centrifugal force at the tips of the pear-shaped containers used as reaction flasks. It was assumed from a comparison of laboratory results, using this and the A.O.C.S. method, that the centrifugal laboratory method will more closely approach the results of plant refining. The type of oil had much less influence on the losses obtained with the analytical centrifuge than with the modified cup method.

In applying the suggested centrifugal procedure to the refining of laboratory samples of extracted soybean oils, certain changes in the equipment were made in this laboratory which facilitated the handling of the oil and which appeared to give uniform and reliable results. The procedure outlined below appears to fulfill the need for a rapid, accurate, and simple refining method for the evaluation of soybean oils. The results obtained in routine laboratory investigations are submitted in the nature of a progress report in order to illustrate the applicability of the method in the separation of neutral oil from the compacted soap stock. No attempt has been made in this preliminary work to correlate bleach color with refining loss. In all cases the refined oils were light in color and appeared satisfactory for further processing. An International Centrifuge Size 1-SB, equipped with International Head, Cat. No. 277 and two bronze tunion cups, is used in the following procedure for the separation of the oil and soap stock.

Procedure

Two hundred grams of oil are weighed into each of two pressed glass centrifuge cups (250 ml. capacity). The cups are supported for weighing in tared 400 ml. beakers which are marked to identify them with the respective cups in all subsequent weighings. Cups containing oil are set in strap iron cages and then placed in a water bath at 68-75°F. The oil is stirred by means of air stirrers equipped with figure 8 propellors (½ x 1¼"). Twenty or 24°Bé alkali solution, equal to the amount required to neutralize the free fatty acid in the oil plus 100% excess, is weighed into tared 25 ml. beakers. (An allowance of 0.04 grams of caustic solution usually compensates for the solution which does not drain from the beaker.) The caustic is quickly added to the rapidly stirred oil. Stirring is continued at moderate speed for 30 minutes. At the end of this period the centrifuge cup, stand, and stirring assembly are transferred to a second bath which is maintained at 145-152°F. The oil and foots are stirred slowly for 20-30 minutes to coagulate the soap stock. At the end of this period the stirrers are raised, excess oil and other material removed from the blades and replaced in the glass cups. The glass cups are placed in the bronze trunion cups of the centrifuge. The oil and foots are centrifuged in an International Centrifuge for 30 minutes at 2,500-3,000 R.P.M. The cups are reweighed to determine evaporation loss and the oil decanted into the matching tared beaker. The cups are inverted on a wooden draining rack and allowed to drain for at least 30 minutes into their respective beakers. Adhering oil is scraped from the sides of the cups by means of small spatula and transferred to the beaker containing the drained oil. Calculation of refining loss is made by the two usual methods, a) difference between weight of crude and weight of refined oils, b) weight of soap stock plus evaporation loss minus weight of NaOH solution. Both calculations are generally made and the average result expressed as the refining loss. Figure A. shows the equipment used and the oil at various stages of the refining operation. The draining of the finished oil on the left illustrates the compactness of the "foots" and the ease and efficiency of the removal of neutral oil. Duncan (8), in a recent publication which came

FIG. A. Equipment used in the Refining Operation.

to the author's attention during the preparation of this manuscript, has also used the glass centrifuge cups in the refining of trichlorethylene extracted oils.

Discussion

The results reported herein are those which have been obtained during the past several years on the refining of various laboratory samples. Data presented in Table I were on extracted degummed soybean oils of free fatty acid content from 0.15 to 0.45%. Similar data are presented in Table 2 on the refining of undegummed extracted oil of free fatty acid contents from 0.43 to 0.57%.

TABLE I

Refining Loss of Degummed Soybean Oils*

Number of Determinations	F.F.A. %	Refining Loss		Standard Deviation
		Average %	Range %	
10	0.15	0.81	0.40	0.119
20	0.19	0.94	0.53	0.101
9	0.25	1.22	0.46	0.133
9	0.27	1.37	0.23	0.082
6	0.29	1.42	0.09	0.028
8	0.30	1.46	0.15	0.048
6	0.45	1.73	0.26	0.086
Grand Average			0.30	0.085

*100% excess 20°Bé Caustic.

TABLE 2

Refining Loss of Undegummed Soybean Oil *

Number of Determinations	F.F.A. %	Refining Loss		Standard Deviation
		Average %	Range %	
4	0.43	2.63	0.18	0.068
4	0.49	2.91	0.03	0.020
4	0.54	2.81	0.34	0.140
4	0.55	3.09	0.15	0.054
4	0.57	3.12	0.28	0.099
Grand Average			0.19	0.076

* 100% excess 20°Bé Caustic.

Twenty degree Baumé alkali in 100% excess was used in the above refinings. Refining loss showed a progressive rise with increase in free fatty acid content of the crude oils. The foots in all cases were solid, affording ready removal of the clear refined oil by decantation. No remelts were considered necessary. Standard deviation for the refining of the degummed oils ranged from 0.028 to 0.133 with a grand average value of 0.085. Standard deviation for refining of the undegummed oils ranged from 0.020 to 0.140 with a grand average value of 0.076. While no correlation can be made between the refining losses of the degummed and undegummed oils, it is apparent that "break" materials in the latter oils contribute materially to the higher losses.

TABLE 3

Effect of Varying Excess Caustic on the Refining Loss of Soybean Oil *

Number of Determinations	Excess Over Theory** %	Refining Loss		Standard Deviation
		Average %	Range %	
4	100	0.67	.01	0.007
6	75	0.61	.05	0.046
4	50	0.57	.08	0.37
4	25	0.49	.03	0.010
4	15	0.45	.06	0.025
4	10	0.44	.03	0.012
2	5	0.42	.02	0.010
2	1	0.42	0	0

* F.F.A. 0.24%.
** 8.6% Custic.

Data presented in Table 3 and illustrated graphically in Figure 1 give the results of refining a degummed oil (F.F.A. — .24%), using 8.6% alkali in excesses of from 1-100%. Table 4 and Figure 2 give similar data on the refining of the same oil using 13% alkali. Samples were run in pairs. The individual results as well as averages of duplicates by both methods of calculation are in good agreement. Progressive increase in refining loss is noted as percent excess of caustic is increased. No trouble was encountered in draining the oil from the compact foots. Table 5 shows the comparison of refining loss of sev-

TABLE 4

Effect of Varying Excess Caustic on the Refining Loss of Soybean Oil *

Number of Determinations	Excess Over Theory** %	Refining Loss		Standard Deviation
		Average %	Range %	
4	100	0.80	0.09	0.092
6	75	0.67	0.10	0.030
6	50	0.65	0.16	0.180
4	25	0.57	0.20	0.078
4	15	0.52	0.21	0.082
4	10	0.46	0.08	0.033
2	5	0.41	0.01	0.002
2	1	0.43	0.08	0.040

* F.F.A. 0.24%.
** 13.0% Caustic.

TABLE 5

Comparison of Refining Loss by Centrifuge and Official Methods

Oil	F.F.A.	Alkali* °Bé	Refining Loss	
			Centrifuge %	Official %
1.	0.28	24	1.72	3.3
2.	0.35	30	1.06	3.1
3.	0.36	20	1.21	3.4
	0.36	24	1.42	3.4
4.	0.37	24	1.67	2.1

* 100% excess.

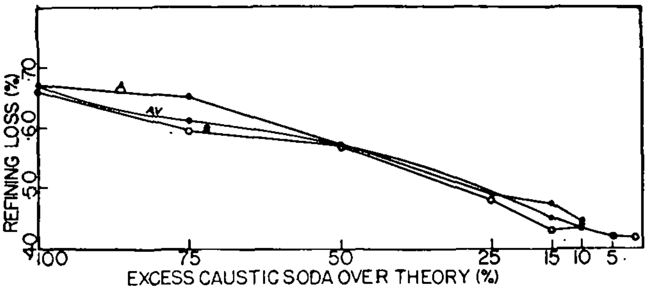

FIG. 1. Refining of soybean oil with 8.6% caustic soda.

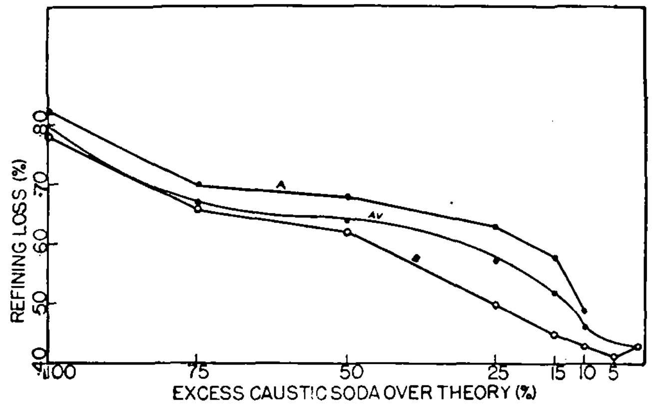

FIG. 2. Refining of soybean oil with 13% caustic soda.

eral oils by the laboratory centrifuge method and the Official Method (Commercial Laboratory). In all cases the losses are considerably lower by the centrifugal method.

Summary

A centrifugal method is presented for the determination of refining loss of extracted soybean oils, entailing modifications of a procedure first introduced by the Swift and Company Research Laboratories and later improved by the Regional Soybean Laboratory. The method using glass cups in the International Centrifuge permits speed and accuracy in the laboratory refining of extracted soybean oils.

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Tangerine Seed Oil[1]

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A KNOWLEDGE of the chemical and physical properties of citrus seed oils is of importance for two practical reasons. One of these, of course, is concerned with the possible commercial uses of the oils when they are recovered in quantity as by-products of the canning industry. The other, and less obvious, reason is due to the possibility that the storage life of canned citrus juices is affected by the small amounts of the seed oils that get into them during the extraction process. Some evidence in support of this possibility was obtained by Nolte and von Loesecke (1) who showed that the lipids from orange juice that had deteriorated on storage gave positive tests for rancidity while those from fresh juice did not. Their work did not exclude the possibility that the lipids were oxidized preferentially while serving as antioxidants. Furthermore, it dealt with the whole lipid fraction of the juice, only a part of which was derived from seeds. Nevertheless, as part of an investigation of citrus juice lipids, a fairly detailed analysis of a seed oil seemed warranted and the results are reported below. Tangerine seed oil was chosen because no work on it had come to the author's attention and because, with the analysis of it in hand, any marked differences in its properties and composition from those obtained by other workers on other citrus seed oils would be apparent. The storage life of canned tangerine juice was known to be shorter than that of either canned orange or grapefruit juices, and this fact was thought to lend special significance to any differences found in the oils which might furnish an explanation of the different keeping qualities of the juices and the nature of the deterioration.

Experimental

Seeds of the Dancy tangerine (*Citrus nobilis* var. *deliciosa*) were obtained directly from the finisher at a cannery in Florida during the 1947-48 season. Most of the pulp was eliminated by stirring with large volumes of water and decanting. The seeds were then air-dried by spreading on a floor in front of a fan. After hand-sorting to remove broken seeds and fragments of pulp, the weight was 7.7 kg. The seeds were ground in a hammer mill and then in a food chopper. A small amount of oil (referred to in Table V as "cold-pressed" oil) was obtained as the seeds were passed through the food chopper and was treated separately in determining the chemical and physical properties. The bulk of the oil was obtained by extracting the ground seeds with acetone and then regrinding and re-extracting. A final extraction of the ground seeds was made with petroleum ether. The acetone extracts were evaporated and the petroleum ether extract was added and all of the solvent was evaporated by heating in vacuum. The entire yield on the basis of the air-dried seeds was 26.6%. The chemical and physical properties of the oils are given in Table V, standard methods of analysis being used throughout. In the determination of all thiocyanogen values the recommendations of Lambou and Dollear (2, 3) were followed closely.

To obtain the free fatty acids, 300 g. of the solvent-extracted oil were refluxed for six hours with 1,500 ml. of 95% ethanol and 180 g. of potassium hydroxide. After distilling off about half of the ethanol and diluting the remaining mixture with 1.5 volumes of water, the unsaponifiable matter was removed by extracting for 67 hours in a continuous liquid-liquid extractor with 30°-65° petroleum ether. The extract was washed thoroughly with potassium hydroxide solution and water, dried over anhydrous sodium sulfate, and set aside for possible later examination. The washings were added to the main solution of fatty acids soaps which was then acidified with dilute (1 + 3) sulfuric acid and again thoroughly extracted with petroleum ether using separatory funnels. The extract was washed with water, dried over anhydrous sodium sulfate, filtered into a flask, and the solvent distilled off under vacuum. A water bath was used as the source of heat throughout and nitrogen gas was bled into the system to prevent bumping. The yield of acids was 287 g., or 95.6%.

No attempt was made to separate the fatty acids into saturated and unsaturated fractions before esterification, the writer preferring to make saturated acid determinations on the individual ester fractions after distillation. The esterification was carried out by refluxing 255 g. of the mixed acids with 1 liter of absolute methanol and 9 ml. of concentrated sulfuric acid for five hours. The excess methanol was distilled off and the mixture of esters was dissolved by ethyl ether, washed with water, 10% sodium carbonate solution, and again thoroughly with water after which it was dried with sodium sulfate and the

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[1] Agricultural Chemical Research Division Contribution No. 241.

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